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Investigation on the production of copper nitride (copper azide) thin films and their nanostructures

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Abstract

Copper thin films of 80-nm thickness were deposited on glass substrate using electron beam deposition at two different deposition angles of 0° and 40°, and they were post-annealed under flow of nitrogen at different temperatures. The structure of the films was analyzed using X-ray diffraction, atomic force microscope, and scanning electron microscope. Investigation on the copper nitride phase formation showed that this phase was not formed in the samples produced at 0°, while those prepared at oblique angle of 40° clearly showed the formation of copper azide phase. This is related to the porosity of the film structure, hence increased surface area for the reaction of nitrogen with copper atoms. Therefore, this is a simple method for preparation of copper nitride films that are not usually formed due to low reactivity of copper (as transition metal) with nitrogen. The results showed that the crystallite size (coherently diffracting domains), grain size, and surface roughness increase with annealing temperature.

Keywords: Copper nitride, Thin film, Electrical resistance, Oblique angle deposition

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Introduction

During the last half a century, extended studies have been carried out on transition metal nitrides (MN_x). Most of these studies have been concentrated on the thermodynamical stability of nitrides obtained from metals in groups 3 to 6. For example, nitrides of groups 4 and 5 such as NbN, ZrN, and TiN usually are formed at temperatures above 1,000°C when the metal reacts with N_2 or NH_3 [1]. In recent years production of transition metals in a form of nitride has been of high interest to the researches because of their physical properties such as hardness and high melting point as well as their applications in different industries and day to day implementations. The reactivity of transition metals with 3D electronic structure (i.e., Ti, Cr, Fe, Co, Ni, and Cu) with nitrogen decreases when increasing their atomic number, hence, the reactivity of copper with nitrogen among the above-mentioned transition metals is the lowest. One may obtain copper nitride via substituting reactions such as CuF_4 or NH_4F. The density of the produced samples is 5.84 gr/cm^3 and their molecular weight is 204.63. Maruyama [2] reported that in a time laps of 15 months, copper nitride under the condition of 95% humidity and temperature of 60° did not show any change in its structural characteristics and optical properties. Hence, owing to its stability in room temperature, it has found important applications in industry. For the application of copper nitride, one may mention its use as a material for information memory in optical disks which benefits from its high capacity, long life time, and low cost and weight when compared with other materials. It can also be used in high speed integrated circuits [3]. Different methods have been implemented to produce copper nitride thin films such as DC reactive magnetron sputtering [4-6], RF reactive magnetron sputtering [7-10], molecular beam epitaxy [11,12], and pulsed laser deposition [13]. In this work we report a simple method for production of copper nitride thin film in which we have taken the advantage from the porosity of the film deposited at an oblique angle.

Experimental details

Copper films of 80 nm thickness were deposited on glass substrates (18 × 18 × 1 mm) using electron beam evaporation at room temperature and at two different deposition

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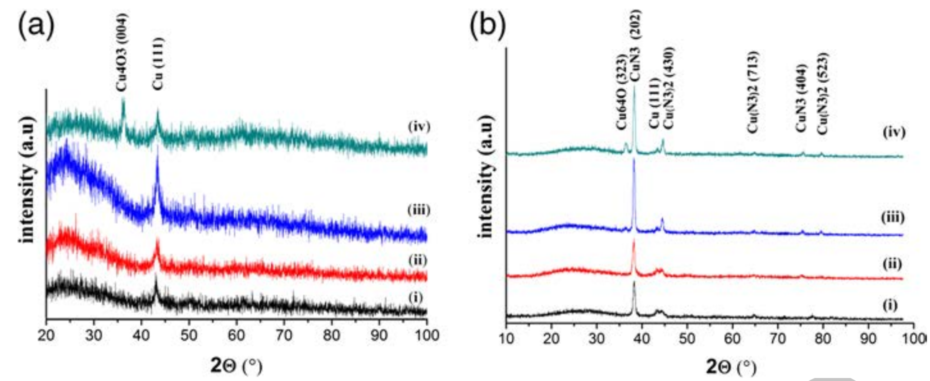

Figure 1 XRD patterns of samples deposited at 0° (a) and XRD patterns of samples deposited at 40° (b).

angles of 0° and 40° with respect to the substrate surface normal. A deposition rate of 0.2 Å/s was used. The purity of copper was 99.98%. An Edwards (Edwards E19 A3) coating plant with a base pressure of 2×10^{-7} mbar was used. Prior to deposition, all substrates were ultrasonically cleaned in heated acetone then ethanol. The distance between the centre of the evaporation boat and the substrate holder disk was 20 cm. Post-annealing of the Cu/Glass films were performed at four different temperatures of 373, 453, 533, and 613 K in nitrogen environment with a flow rate of 500 sccm. The crystallographic structure of these films was obtained using a Bruker D8 Advance X-ray Diffractometer (CuKα radiation) with a step size of 0.02° and count time of 1.5 s per step, while the surface physical morphology/nanostructure and roughness was obtained by means of AFM (Auto probe PC, Park Scientific Instrument, USA; in contact mode, with a low stress silicon nitride tip of less than 200 Å radius and a tip opening of 18°) analysis and field emission scanning electron microscope (FESEM; Hitachi S-4100 SEM, Japan). The deposition process was repeated several times and the samples were used at different stages of this work produced consistent results within the logical experimental achievements at each stage.

Results and discussion

X-ray diffraction

Figure 1a shows the X-ray diffraction (XRD) patterns obtained for four samples deposited at normal angle to the substrate surface and annealed with flow of nitrogen. All patterns show a preferred orientation for the Cu (111) crystallographic orientation. This is expected since Cu has an fcc structure and the (111) facet has the lowest surface energy. The intensity of this preferred orientation is increased with the annealing temperature, with the exception at 613 K annealing temperature that can be due to the formation of an extra peak related to copper oxide as Cu_4O_3 (004) as a result of the fact that oxide becomes stable at higher temperature thermodynamically. Figure 1b shows comparative patterns of XRD analysis for four samples deposited at 40° with respect to the substrate surface normal annealed at four different temperatures with flow of nitrogen. An increase of peak intensity with temperature, in particular, for the CuN3 (202) up to 553 K can be distinguished; while at higher temperature of 613 K, the intensity of this peak is slightly reduced. This may be due to the formation of $Cu_{64}O$ (323) phase at this annealing temperature. In addition it can be observed that at all of annealing temperatures other compositions of copper nitride, namely $Cu(N_3)_2$ (430), $Cu(N_3)_2$ (523), $Cu(N_3)_2$ (713), and CuN_3 (404), are also formed with lower intensities.

The crystallite size, *D* (coherently diffracting domains), is obtained using the Scherrer formula [14]:

$$B = \frac{k\lambda}{D\cos\theta} \qquad (1)$$

where, λ is the wavelength of X-ray, *θ* is the Bragg angle, and *k* is a dimensionless constant which is related to the

Table 1 Details of the information obtained from the XRD patterns of samples deposited at 0°

Annealing temperature (K)	2Θ (deg)	2Θ JCPDS (deg)	Intensity (a.u.)	FWHM (deg)	Crystallite size (nm)	Diffraction line	JCPDS card number
373	43.18	43.29	14.16	1.0886	8.0	Cu(111)	4-836
453	43.28	43.29	19.96	0.9096	9.0	Cu(111)	4-836
533	43.34	43.29	26.44	0.4723	19.0	Cu(111)	4-836
613	43.36	43.29	18.42	0.5937	15.0	Cu(111)	4-836

Table 2 Details of the information obtained from the XRD patterns of samples deposited at 40°

Annealing temperature (K)	2Θ (deg)	2Θ JCPDS (deg)	Intensity (a.u.)	FWHM (deg)	Crystallite size (nm)	Diffraction line	JCPDS card number
373	38.22	38.28	85	0.5292	16.0	CuN_3 (202)	85-903
453	38.22	38.28	101.66	0.5152	17.0	CuN_3 (202)	85-903
533	38.18	38.28	184.84	0.4228	21.0	CuN_3 (202)	85-903
613	38.32	38.28	167.82	0.4647	19.0	CuN_3 (202)	85-903

shape and distribution of crystallites (usually taken as unity) [15]. For obtaining the value for B, we used the usual procedure of full width at half maximum (FWHM) measurement technique [16]; therefore,

$$B = \left(W_0^2 - W_i^{2i}\right)^{1/2}, \tag{2}$$

where W_0 is the FWHM of the sample and W_i is the FWHM of stress free sample (standard SiO_2 single crystal sample). The crystallite size, D (coherently diffracting domains) variation obtained from Cu(111) peak in the case of films deposited at 0° and from CuN_3 (202) line for films deposited at 40° deposition angles are given in Tables 1 and 2. Results show that in case of 0° deposition angle, the value of D increases from 8 (lowest annealing temperature) to 19 nm (533 K as annealing temperature) and then at highest temperature of 613 K, it decreases to 15 nm; while for 40° deposition angle, the lowest value is 16 nm which increases to 21 nm at 533 K and then at 613 K, it again reduces to 19 nm. These observations are consistent with the variation of peak intensity in Figure 1a,b as discussed above.

SEM and AFM (nanostructure)

The surface morphology of the samples prepared at four different annealing temperatures was analyzed using field emission scanning electron microscope (FESEM) and atomic force microscope (AFM). Figure 2a,b shows the deposited copper thin film SEM images (surface and cross section) for 0° and 40° deposition angles, respectively, before annealing with flow of nitrogen. It can be clearly observed that the film deposited at 0° consists of tapered structure with almost 90° rise angle, while film deposited at 40° consists of similar structure but with a tilted angle (rise angle) of about 23° in agreement with the well-known tangent rule (tan α = 2 tan β) [17]. It can also be seen that the film produced at oblique angle contains high level of pores (voids) between grains which is due to the

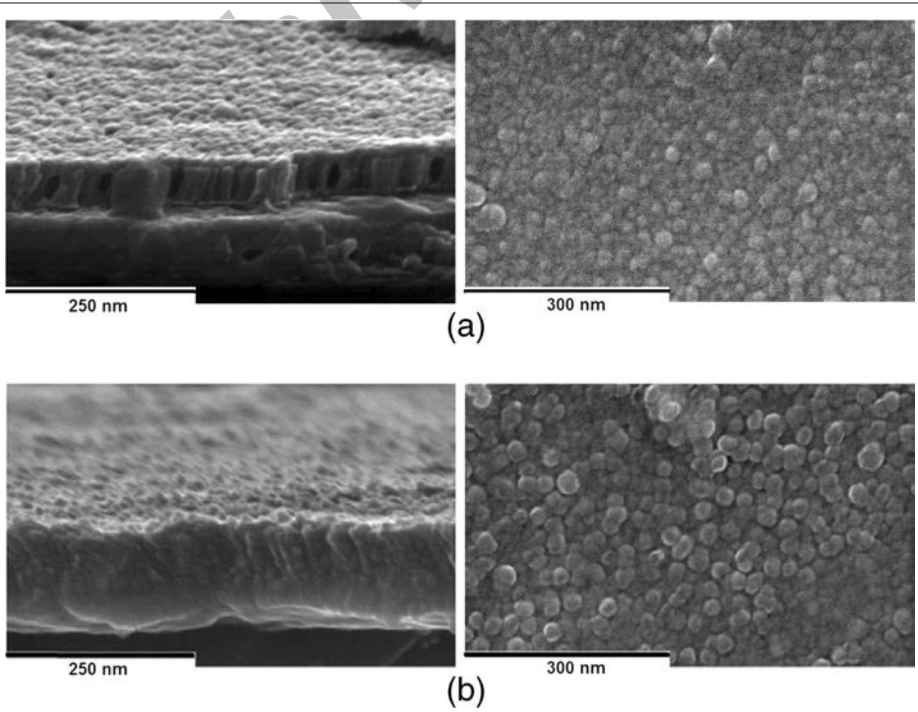

Figure 2 Deposited copper thin film SEM images for 0° and 40° deposition angles. (**a**) Surface and cross-section FESEM images of samples deposited at 0° incident angle (**b**) Surface and cross-section FESEM images of samples deposited at 40° incident angle.

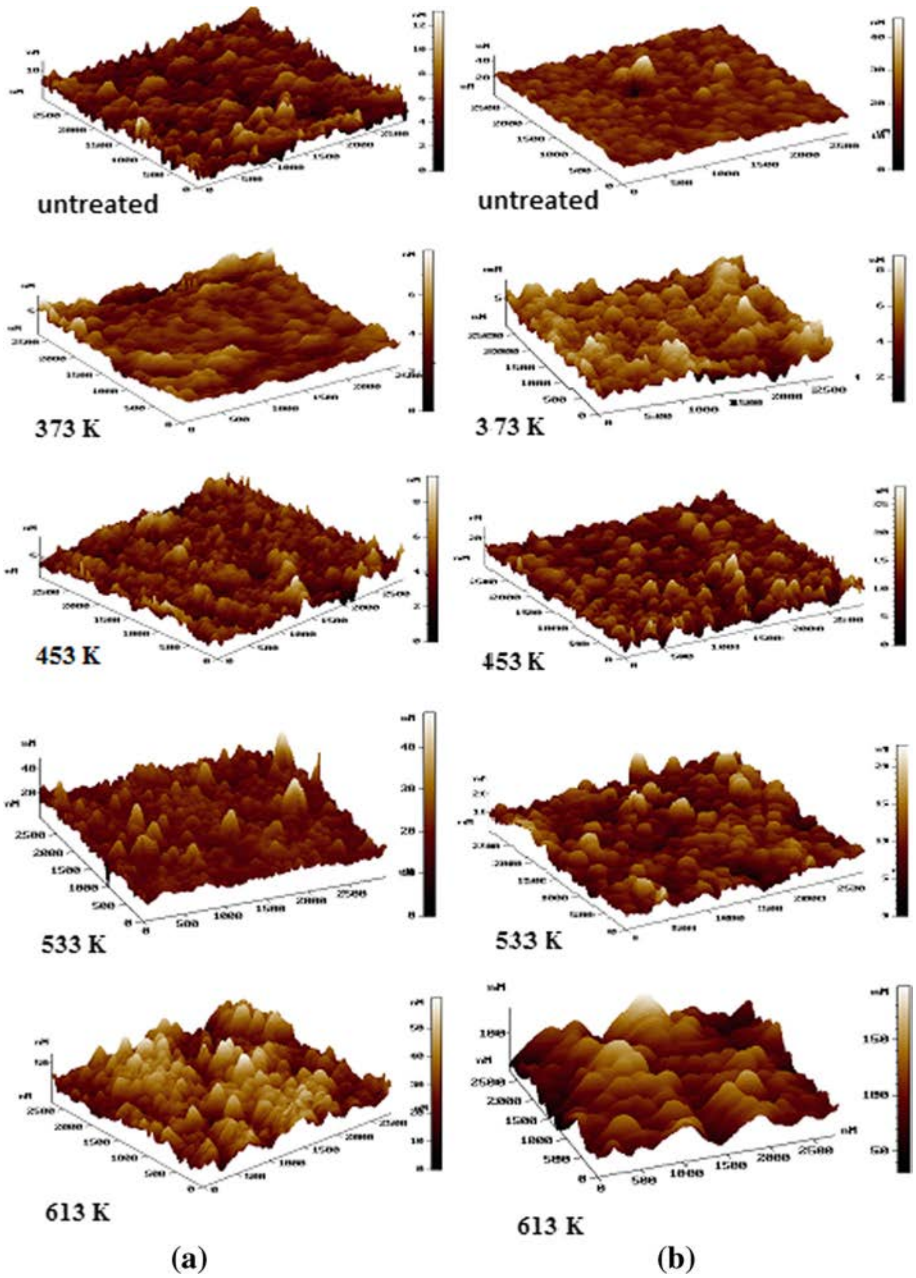

Figure 3 3D AFM images of samples deposited at 0° (a) 3D AFM images of samples deposited at 40° (b).

Table 3 Details of the information obtained from the AFM images of samples deposited at 0°

Annealing temperature (K)	Grain size (nm)	Roughness (nm)
Untreated	45.5	1.38
373	57.0	0.59
453	43.5	0.78
533	47.5	2.34
613	71.0	7.11

Table 4 Details of the information obtained from the AFM images of samples deposited at 40°

Annealing temperature (K)	Grain size (nm)	Roughness (nm)
Untreated	55.0	3.64
373	41.5	1.03
453	38.0	2.50
533	53.0	2.87
613	86.0	18.24

shadowing effect. We have used this phenomenon to, in fact, penetrate the nitrogen molecules between grains while they provide a much higher surface area than the grains in film deposited at 0° deposition angle; hence, higher reaction rate between nitrogen molecules and copper atoms has resulted in the copper nitride phase formation as discussed in the previous section regarding XRD patterns (Figure 1).

Figure 3a,b shows the 3D AFM images of samples deposited at 0° and 40° angles annealed at different temperature. In case of the samples deposited at 0° angle, one may distinguish a few columnar structures between smaller grains in the AFM image of untreated sample. These structures may be responsible for the small peak observed in the XRD pattern for Cu(111). At 373 K a more uniform morphology is obtained that according to the XRD pattern of this sample, higher number of Cu (111) domains should have formed. The formation of Cu (111) domains is continued at higher temperature of 533 K, and AFM image shows larger grains (columnar structures) consistent with XRD result (Figure 1a and Table 1). When the annealing temperature is increased to 613 K, the film surface morphology changed which may be the result of formation of Cu_4O_3(004) and Cu (111) as discussed in the XRD section.

Regarding the samples deposited at 40° angle, the untreated sample shows columnar grains that are distributed on the surface almost evenly. At lowest annealing temperature (373 K) with flow of nitrogen, one may distinguish the distribution of very small grains among larger grains. A comparison of this figure with that of the untreated sample clearly shows the effect of annealing procedure on the morphology of these films. If these observations are compared with the XRD results, it may be deduced that the large columnar grains in the annealed sample belong to the CuN_3(202) phase of the copper nitride. By increasing the annealing temperature to 453 K, larger (individually formed) columnar grains with some smaller, but again columnar structure grains between larger grains can be seen. Again XRD results suggest that as the intensity of CuN_3(202) is increased in this case relative to the lower annealing temperature; all these structures should belong to the CuN_3(202). At 533 K annealing temperature, yet again larger grains are formed indicating the higher population of CuN_3(202) crystals (domains). Finally, at the highest annealing temperature (613 K) very large grains are formed. Examination of the morphology of our samples in obtaining surface roughness and average grain size showed that both surface roughness and average grain size increase with annealing temperature (see Tables 3 and 4). The exception for grain size is the lowest annealing temperature. The reason for this could be the onset of copper nitride formation. The reaction between nitrogen and copper atoms can change the pattern of grains. The reason for the increase of the surface roughness with annealing temperature could be the formation of larger grains, due to diffusion effect, which follows with the formation of valleys between them. As the temperature increases, larger grains are formed (enhanced diffusion effect) with deeper valleys between them that in extreme case, these valleys may extend to the substrate surface and one may observe the grooving effect [18,19].

Conclusions

In order to produce copper nitride thin films, a simple method was investigated by means of oblique angle deposition of copper thin films and subsequent annealing with flow of nitrogen gas at different temperatures. The oblique angle deposition provides us with films of high porosity; hence, higher film surface can be obtained relative to deposition at normal angle which, in turn, facilitates the reaction between copper atoms and nitrogen. Comparison of the films produced at normal angle to the substrate surface and films deposited at 40° oblique angle clearly resulted in copper nitride formation in the latter films, while no sign of nitride film was observed in the former samples. The structure of the films was analyzed by means of XRD, AFM, and FESEM. Therefore, in this paper we have reported a simple method for the preparation of copper nitride films that are not usually formed due to low reactivity of copper (transition metal) with nitrogen. The results showed that the crystallite size (coherently diffracting domains), grain size, and surface roughness increase with annealing temperature.

Competing interest
The authors declare that have no competing interests.

Authors' contributions
Both authors read and approved the final manuscript.

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